

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 17/00, D21H 17/69 // B01F 17/00	A1	(11) International Publication Number: WO 95/25146 (43) International Publication Date: 21 September 1995 (21.09.95)
(21) International Application Number: PCT/GB95/00563 (22) International Filing Date: 16 March 1995 (16.03.95) (30) Priority Data: 9405275.0 17 March 1994 (17.03.94) GB (71) Applicant (for all designated States except US): ECC INTERNATIONAL LIMITED [GB/GB]; 1015 Arlington Business Park, Theale, Reading RG7 4SA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): EAGLES, Warren, Paul [GB/GB]; 3 Cumberland Road, Loughborough, Leicestershire LE11 0DE (GB). ROGAN, Keith, Robert [GB/GB]; 10 Roche Road, Bugle, St. Austell, Cornwall PL26 8PW (GB). SKUSE, David, Robert [GB/GB]; 49 Midway Drive, Truro, Cornwall TR1 1NQ (GB). (74) Agent: NASH, David, Allan; Haseltine Lake & Co., Hazlitt House, 28 Southampton Buildings, Chancery Lane, London WC2A 1AT (GB).		(81) Designated States: AU, BR, FI, GB, JP, KR, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: AQUEOUS SUSPENSIONS OF INORGANIC MATERIALS (57) Abstract There is disclosed a process for improving the rheological properties of an aqueous suspension of a particulate inorganic material which comprises the steps of: (a) forming an aqueous suspension of the particulate inorganic material and an effective amount of an anionic polyelectrolyte dispersing agent; (b) diluting the suspension formed in step (a) with water to give a solids concentration of not less than 20 % by weight of the particulate inorganic material; and (c) reconcentrating the diluted suspension formed in step (b) to give a solids concentration of at least 50 % by weight of the particulate inorganic material.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

AQUEOUS SUSPENSIONS OF INORGANIC MATERIALS

This invention relates to a method for preparing a rheologically stable, concentrated aqueous suspension of a finely divided particulate inorganic material, particularly a finely divided particulate natural or
5 synthetic mineral material, such as a clay or an alkaline earth metal carbonate pigment.

It is often advantageous to produce and distribute mineral pigment or filler materials, especially to the
10 paper and water based paints industries, in the form of a concentrated suspension in water. A user receiving a mineral material in this form is able to avoid the high energy and capital costs which would be involved in the mixing of a dry material with water to form a
15 suspension on his own premises, and, if the mineral material is produced by a wet route, the producer is able to avoid the costs of complete drying of the material. A concentrated aqueous suspension is also easy to handle and convey, and presents no dust
20 problem.

The rheological properties of an aqueous suspension of a particulate inorganic material depend upon a number of factors including the concentration of solid material in the suspension, the particle size
25 distribution of the solid material, as indicated, for example, by the median particle diameter of the distribution, and the type and amount of dispersing agent which is used. Generally, a suspension becomes more viscous, or less fluid, as the solids
30 concentration is increased, or as the median particle diameter of the particle size distribution is reduced. Also there is an increasing tendency for the suspension to become more viscous with time on storage. Assuming that an effective dispersing agent for the inorganic
35 material is available, it is generally found that there is an optimum amount of the dispersing agent which must

-2-

be added to the suspension to give maximum fluidity and maximum rheological stability, other factors being kept the same.

According to a first aspect of the present invention, there is provided a process for improving the rheological properties of an aqueous suspension of a particulate inorganic material which comprises the steps of:

(a) forming an aqueous suspension of the particulate inorganic material and an effective amount of an anionic polyelectrolyte dispersing agent;

(b) diluting the suspension formed in step (a) with water to give a solids concentration of not less than 20% by weight of the particulate inorganic material; and

(c) reconcentrating the diluted suspension formed in step (b) to give a solids concentration of at least 50% by weight of the particulate inorganic material.

The suspension formed in step (c) is suitable for transportation and/or use without the addition of a further quantity of dispersing agent.

Steps (b) and (c) of the process of the invention may advantageously be repeated one or more times.

The suspension formed in step (a) preferably contains at least 50%, and preferably at least 60% by weight of the particulate inorganic material.

In step (a), the particulate inorganic material is typically a natural or synthetic mineral material. The invention has been found to be particularly suited to the treatment of paper coating pigments, paper fillers or pigments or extenders for use in water-based paints. The particulate mineral material may advantageously be kaolin clay or calcium carbonate. Generally the particulate inorganic material will have a particle size distribution such that at least 45% by weight, and preferably at least 50% by weight, of the particles

-3-

have an equivalent spherical diameter smaller than $2\mu\text{m}$.

The anionic polyelectrolyte is typically used in an amount of at least 0.05% by weight, based on the weight of the particulate inorganic material, although
5 the optimum amount to achieve dispersion of the inorganic material can be determined by the skilled person without difficulty. The anionic polyelectrolyte dispersing agent is advantageously a water soluble salt of poly(acrylic acid) or of poly(methacrylic acid)
10 having a weight average molecular weight of not more than 20,000, as determined by gel permeation chromatography using a low angle laser light scattering detector. The anionic polyelectrolyte dispersing agent may, for example, be an alkali metal (for example
15 sodium) or ammonium salt of a poly(acrylic acid) or a poly(methacrylic acid). Sodium polyacrylate having a weight average molecular weight in the range from 1,000 to 10,000 is especially suitable. The amount of the anionic polyelectrolyte dispersing agent used is
20 advantageously in the range of from 0.1 to 2.0% by weight, based on the weight of the particulate inorganic material.

The anionic polyelectrolyte is typically fully neutralised. However, it is within the scope of the
25 present invention for the anionic polyelectrolyte to be partially neutralised (cf. EP-A-0100948).

In step (b), the suspension is preferably diluted so as to reduce the solids concentration by at least 5 percentage points. It is also preferred that the
30 suspension is not over-diluted as this has been found to give unacceptable results, as well as being undesirable from an economic point of view; thus, the solids concentration should preferably not be reduced below about 30% by weight of the particulate inorganic
35 material. Typically, the suspension will be diluted to a solids concentration in the range of from 30% to 70%

-4-

by weight, more preferably to a solids concentration in the range of from 30% to 60% by weight.

In step (c), the diluted suspension is preferably reconcentrated by means of a centrifuge, such as a high speed centrifuge or by means of a filtration device such as a membrane filtration device of the type described, for example, in United States Patent Specification No. 5223463. The membrane filtration device may be, for example, of the plate and frame, tubular or spiral type. There is no requirement in reconcentration step (c) for a flocculating agent to be added.

In step (c) it is preferred to reconcentrate the diluted suspension formed in step (b) to give a solids concentration of at least 60% by weight of the particulate inorganic material.

It is found that, by the process of the invention, the viscosity of a suspension of a finely divided, particulate inorganic material, for a given solids concentration, median particle diameter of the inorganic material and dose of dispersing agent is considerably reduced, and the tendency for the suspension to "gel", or increase in viscosity on storage, is also reduced.

In this invention, the percentages by weight of particles having an equivalent spherical diameter smaller than a given value are determined from a particle size distribution curve produced by a SEDIGRAPH particle size analyser.

The invention will now be illustrated, by the following non-limiting examples.

EXAMPLE 1

A sample of a Cornish kaolin clay having a particle size distribution such that 75% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m was suspended in water

-5-

containing 0.3% by weight, based on the weight of the dry kaolin clay, of a sodium polyacrylate dispersing agent having a weight average molecular weight of 4,000 to form a suspension containing 67.7% by weight of dry clay. The suspension was divided into six portions which were diluted with water to solids concentrations of, respectively, 65%, 60%, 55%, 50%, 30% and 10% by weight of dry clay. Each portion was then reconcentrated to a solids concentration of 67.7% by weight of dry clay by removing water in a high speed centrifuge. A further portion was left untreated as a control. The viscosity of each portion of suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 r.p.m. immediately upon the completion of the treatment, and again after storage for 1 hour and 24 hours respectively. The results obtained are set forth in Table 1 below:

Table 1

Diluted Solids concentration (wt.%)	Brookfield Viscosity (Mpa.s) at time (hr.)		
	0	1	24
Control	440	440	470
65	400	420	400
60	320	350	300
55	285	300	260
50	260	275	220
30	280	290	220
10	1440	1440	1340

These results show that the viscosity of the final product suspension of solids concentration 67.7% by weight is lowest, and the suspension has the best rheological stability, when the deflocculated suspension is diluted to 50% by weight before reconcentration to 67.7% by weight. If too much

-6-

dilution water is added, i.e. if the solids concentration is reduced to about 10% by weight before reconcentration, the viscosity of the reconcentrated suspension becomes unacceptably high.

5

EXAMPLE 2

A fine calcium carbonate material having a particle size distribution such that 95% by weight consisted of particles having an equivalent spherical diameter smaller than $2\mu\text{m}$ was prepared in an aqueous suspension having a solids concentration of 75.0% by weight and containing 0.8% by weight, based on the weight of dry calcium carbonate, of the same sodium polyacrylate dispersing agent as was used in Example 1.

The suspension was divided into two portions. One portion was treated in accordance with the invention by the addition of sufficient water to dilute the suspension to a solids concentration of 50% by weight and subsequent reconcentration in the high speed centrifuge to a solids concentration of 75.0% by weight. The other portion was left untreated.

The Brookfield viscosity of the two portions of suspension were determined immediately after preparation, and after standing for 1 hour and 24 hours, respectively, and the results obtained are set forth in Table 2 below:

Table 2

	Brookfield Viscosity (mPa.s) at time (hr.)		
	0	1	24
Untreated	160	310	560
Treated	105	105	110

30

These results show that when an aqueous suspension containing 75% by weight of a fine calcium carbonate material is treated in accordance with the invention, it is possible to form a suspension which not only has

-7-

a lower initial viscosity, but also has a reduced tendency to increase in viscosity on storage, as compared with a suspension prepared in the conventional manner.

5

EXAMPLE 3

A suspension was prepared containing 30% by weight of a Cornish kaolin clay having a particle size distribution such that 75% by weight consisted of particles having an equivalent spherical diameter
10 smaller than $2\mu\text{m}$. The suspension had a pH of 4.5 and contained no dispersing agent. The suspension was divided into two portions. One portion (Portion A) was diluted with sufficient water to double the volume of the suspension and the other portion (Portion B) was
15 left undiluted. Both portions were then partially dewatered by filtration and the resultant filter cakes were dried for 16 hours in an oven at 80°C . Each portion of dried clay was then re-suspended in water containing 0.3% by weight, based on the weight of dry
20 clay, of the same sodium polyacrylate dispersing agent as was used in Example 1, to form a suspension containing 67.7% by weight of the dry clay. The Brookfield viscosity of each suspension was measured immediately after preparation and after standing for 1
25 hour and 24 hours, respectively.

Both suspensions were then treated in accordance with the invention by dilution with water to a solids concentration of 50% by weight of dry clay and subsequent reconcentration to a solids concentration of
30 67.7% by weight by means of the high speed centrifuge. The Brookfield viscosity of each suspension was measured immediately after reconcentration and after standing for 1 hour and 24 hours, respectively. The results are set forth in Table 3 below:

Table 3

	Brookfield Viscosity (mPa.s) at time (hr.)		
	0	1	24
Portion A untreated	760	820	1050
Portion B untreated	880	1040	1425
Portion A treated	370	360	320
Portion B treated	320	330	270

A comparison of the results for "Portion A untreated" and "Portion B untreated" shows that a reduction in the viscosity of the final concentrated, deflocculated suspension can be achieved by diluting with water a clay suspension which contains no dispersing agent and subsequently dewatering the suspension by filtration and re-suspending the dewatered clay in water containing a dispersing agent to form a concentrated product suspension. However, a comparison of the results for "Portions A and B untreated" and "Portions A and B treated" shows that a much greater reduction in viscosity can be achieved by diluting with water, and subsequently reconcentrating, a suspension to which the required amount of dispersing agent has already been added.

EXAMPLE 4

A Cornish kaolin clay having a particle size distribution such that 75% by weight consisted of particles having an equivalent spherical diameter smaller than $2\mu\text{m}$ was suspended in water containing 0.3% by weight, based on the weight of dry kaolin, of the same sodium polyacrylate dispersing agent as was used in Example 1, to form a suspension having a solids concentration of 67.7% by weight. This suspension was divided into two portions. The Brookfield viscosity of one portion was measured immediately after preparation

-9-

and after standing for 1 hour and 24 hours, respectively. The other portion was treated in accordance with the invention by dilution with water to a solids concentration of 50% by weight followed by
5 reconcentration in the high speed centrifuge. By experimentation, the degree of reconcentration which was required to give a concentrated suspension having approximately the same initial Brookfield viscosity as the untreated suspension was determined. The
10 Brookfield viscosity of this suspension after standing for 1 hour and 24 hours, respectively, were also determined. The results obtained are set forth in Table 4 below:

Table 4

	Solids Concn. (% by wt.)	Brookfield Viscosity (mPa.s) at time (hr.)		
		0	1	24
Untreated	67.7	440	440	470
Treated	69.2	400	400	400

These results show that, by treatment in
20 accordance with the invention, it is possible to achieve a deflocculated kaolin suspension which has a higher solids concentration for a given viscosity than an untreated suspension.

EXAMPLE 5

25 A suspension contained 76.0% by weight of a ground calcium carbonate having a particle size distribution such that 95% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m, and 0.8% by weight, based on the weight of dry calcium
30 carbonate, of the same sodium polyacrylate dispersing agent as was used in Example 1. This suspension was divided into two portions. The Brookfield viscosity of one portion was measured immediately after preparation and after standing for 1 hour and 24 hours,

-10-

respectively. The other portion was treated in accordance with the invention by dilution with water to a solids concentration of 50% by weight followed by reconcentration in the high speed centrifuge. By experimentation, the degree of reconcentration which was required to give a concentrated suspension having approximately the same initial Brookfield viscosity as the untreated suspension was determined. The Brookfield viscosity of this suspension after standing for 1 hour and 24 hours, respectively, were also determined. The results obtained are set forth in Table 5 below:

Table 5

	Solids Concn. (% by wt.)	Brookfield Viscosity (mPa.s) at time (hr.)		
		0	1	24
Untreated	76.0	180	450	700
Treated	80.0	385	445	470

These results show that, by treatment in accordance with the invention, it is possible to achieve a deflocculated calcium carbonate suspension which has a higher solids concentration for a given viscosity than an untreated suspension.

EXAMPLE 6

A suspension contained 73.0% by weight of a very finely ground calcium carbonate having a particle size distribution such that 95% by weight consisted of particles having an equivalent spherical diameter smaller than 1 μ m, and 0.8% by weight, based on the weight of dry calcium carbonate, of the same sodium polyacrylate dispersing agent as was used in Example 1. This suspension was divided into two portions. One portion was diluted with water to a solids concentration of 50% by weight and subsequently reconcentrated by means of the high speed centrifuge to

-11-

a solids concentration of 73.0% by weight. The other portion was left undiluted. The Brookfield viscosity of each suspension was measured immediately after formation and after standing for 1 hour and 24 hours, respectively, and the results obtained are set forth in Table 6 below:

Table 6

	Brookfield Viscosity (mPa.s) at time (hr.)		
	0	1	24
Untreated	1980	3290	4800
Treated	420	610	850

10

These results show that, by treatment in accordance with the invention, it is possible to prepare an aqueous suspension containing 73% by weight of a very fine calcium carbonate which suspension has a low initial viscosity and an acceptable increase in viscosity on storage.

EXAMPLE 7

Samples of a Cornish kaolin having a particle size distribution such that 75% by weight consisted of particles having an equivalent spherical diameter smaller than $2\mu\text{m}$ were suspended in water to form suspensions having a solids concentration of 67.7% by weight using amounts of the sodium polyacrylate dispersing agent used in Example 1 which varied from 0.11% by weight to 0.67% by weight. In each case the Brookfield viscosity of the suspension was measured immediately after formation and after standing for 1 hour and 24 hours, respectively.

Each suspension was then diluted with water to a solids concentration of 50% by weight and subsequently reconcentrated by means of the high speed centrifuge to a solids concentration of 67.7% by weight. In each case the Brookfield viscosity of the suspension was

-12-

measured immediately after reconcentration and after standing for 1 hour and 24 hours, respectively.

The results obtained are set forth in Table 7 below:

Table 7

Amount of dispersing agent (wt.%)	Before dilution Brookfield Viscosity (mPa.s) at time (hr.)			After reconcentration Brookfield Viscosity (mPa.s) at time (hr.)		
	0	1	24	0	1	24
0.11	5255	5500	10100	800	1400	2150
0.15	1990	3440	6650	350	510	820
0.19	1420	2700	4050	330	360	370
0.22	880	1200	2200	300	290	250
0.26	800	960	1200	330	330	250
0.30	880	1040	1425	320	330	270
0.37	1100	1220	1600	395	410	340
0.44	1300	1400	1800	570	570	510
0.52	1590	1760	2100	750	790	700
0.59	1920	2040	2500	1050	1070	1000
0.67	2320	2450	2950	1240	1250	1170

5 From the results for the suspensions before treatment in accordance with the invention it is clear that the optimum amount of dispersing agent required to give the minimum viscosity is 0.26% by weight, based on
 10 the weight of dry kaolin. After treatment in accordance with the invention, the optimum amount of dispersing agent is reduced to 0.22% by weight, based on the weight of dry kaolin. Also it can be seen that, after treatment in accordance with the invention, a
 15 suspension which has been deflocculated with 0.15% by weight of the dispersing agent, based on the weight of dry kaolin, has rheological properties which are approximately equivalent to, or better than, those

-13-

given by an untreated suspension which has been deflocculated with 0.26% by weight, based on the weight of dry kaolin, of the dispersing agent.

-14-

CLAIMS:

1. A process for improving the rheological properties of an aqueous suspension of a particulate inorganic material which comprises the steps of:
 - 5 (a) forming an aqueous suspension of the particulate inorganic material and an effective amount of an anionic polyelectrolyte dispersing agent;
 - (b) diluting the suspension formed in step (a) with water to give a solids concentration of not less
10 than 20% by weight of the particulate inorganic material; and
 - (c) reconcentrating the diluted suspension formed in step (b) to give a solids concentration of at least 50% by weight of the particulate inorganic material.
- 15 2. A process according to claim 1, wherein steps (b) and (c) are repeated one or more times.
3. A process according to claim 1 or 2, wherein the suspension formed in step (a) contains at least 50% by weight of said particulate inorganic material.
- 20 4. A process according to claim 1, 2 or 3, wherein said particulate inorganic material is a natural or synthetic mineral material.
5. A process according to claim 4, wherein The particulate mineral material is a kaolin clay or a
25 calcium carbonate.
6. A process according to any one or more of the preceding claims, wherein the particulate inorganic material has a particle size distribution such that at least 50% by weight of the particles have an equivalent
30 spherical diameter smaller than $2\mu\text{m}$.
7. A process according to any one or more of the preceding claims, wherein the anionic polyelectrolyte dispersing agent is a water soluble salt of poly(acrylic acid) or of poly(methacrylic acid) having
35 a weight average molecular weight of not more than 20,000.

-15-

8. A process according to any one or more of the preceding claims, wherein, in step (b), the suspension is diluted so as to reduce the solids concentration by at least 5 percentage points.

5 9. A process according to any one or more of the preceding claims, wherein, in step (b) the dilution is to a solids concentration in the range of from 30% to 70% by weight of the particulate inorganic material.

10 10. A process according to claim 9, wherein, in step (b) the dilution is to a solids concentration in the range of from 30% to 60% by weight of the particulate inorganic material.

15 11. A process according to any one or more of the preceding claims, wherein, in step (c), the diluted suspension is reconcentrated by means of a centrifuge or a filtration device.

20 12. A process according to any preceding claim, wherein, in step (c) the diluted suspension formed in step (b) is reconcentrated to give a solids concentration of at least 60% by weight of the particulate inorganic material.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/00563A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D17/00 D21H17/69 //B01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D D21H B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 154 767 (KUNKLE A.C. ET AL) 13 October 1992 see claim 3 see column 4, line 30 - line 33 see column 5, line 57 - column 6, line 2 ---	1
A	US,A,3 857 781 (MAYNARD R.N.) 31 December 1974 see claim 1 ---	1
A	GB,A,2 019 822 (ALBRIGHT & WILSON LIMITED) 7 November 1979 see claim 1 ---	1
A	WO,A,82 02008 (ANGLO-AMERICAN CLAYS CORPORATION) 24 June 1982 see claims 1,8,13 --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

24 July 1995

Date of mailing of the international search report

31. 07. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Niaounakis, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 95/00563

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,20 30 349 (TATABANYAI SZENBANYAK, TATABANYA) 23 December 1971 see claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/GB 95/00563

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5154767	13-10-92	US-A- 5385239	31-01-95
US-A-3857781	31-12-74	AT-B- 358978	10-10-80
		AU-B- 467409	27-11-75
		AU-A- 5649773	05-12-74
		CA-A- 982161	20-01-76
		DE-A- 2329455	03-01-74
		FR-A- 2188493	18-01-74
		GB-A- 1439679	16-06-76
		JP-A- 49062387	17-06-74
GB-A-2019822	07-11-79	CA-A- 1117845	09-02-82
		SE-B- 442171	09-12-85
		SE-A- 7903753	29-10-79
WO-A-8202008	24-06-82	US-A- 4334985	15-06-82
		EP-A, B 0066611	15-12-82
		US-A- 4468317	28-08-84
DE-A-2030349	23-12-71	NONE	